CONSTRAINING AEROSOL SOURCES AND PROCESSES USING FIELD OBSERVATIONS AND MODELS

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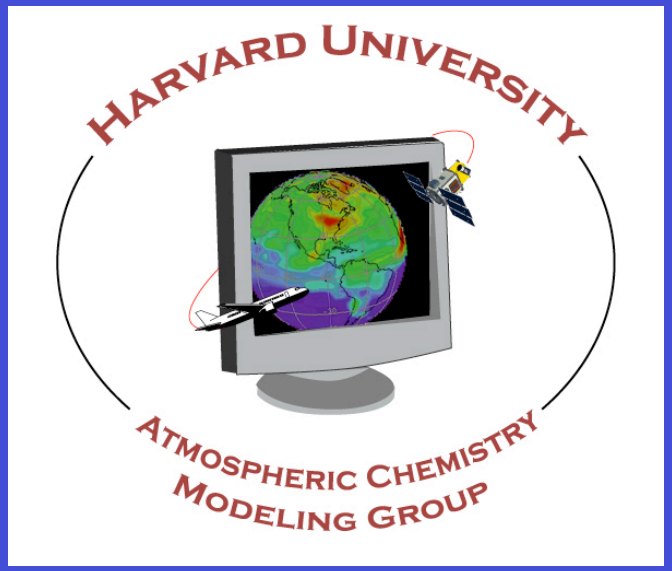
with Tzung-May Fu[1], Jun Wang[2], Easan E. Drury[3]



and funding from EPRI, NSF, NOAA, NASA

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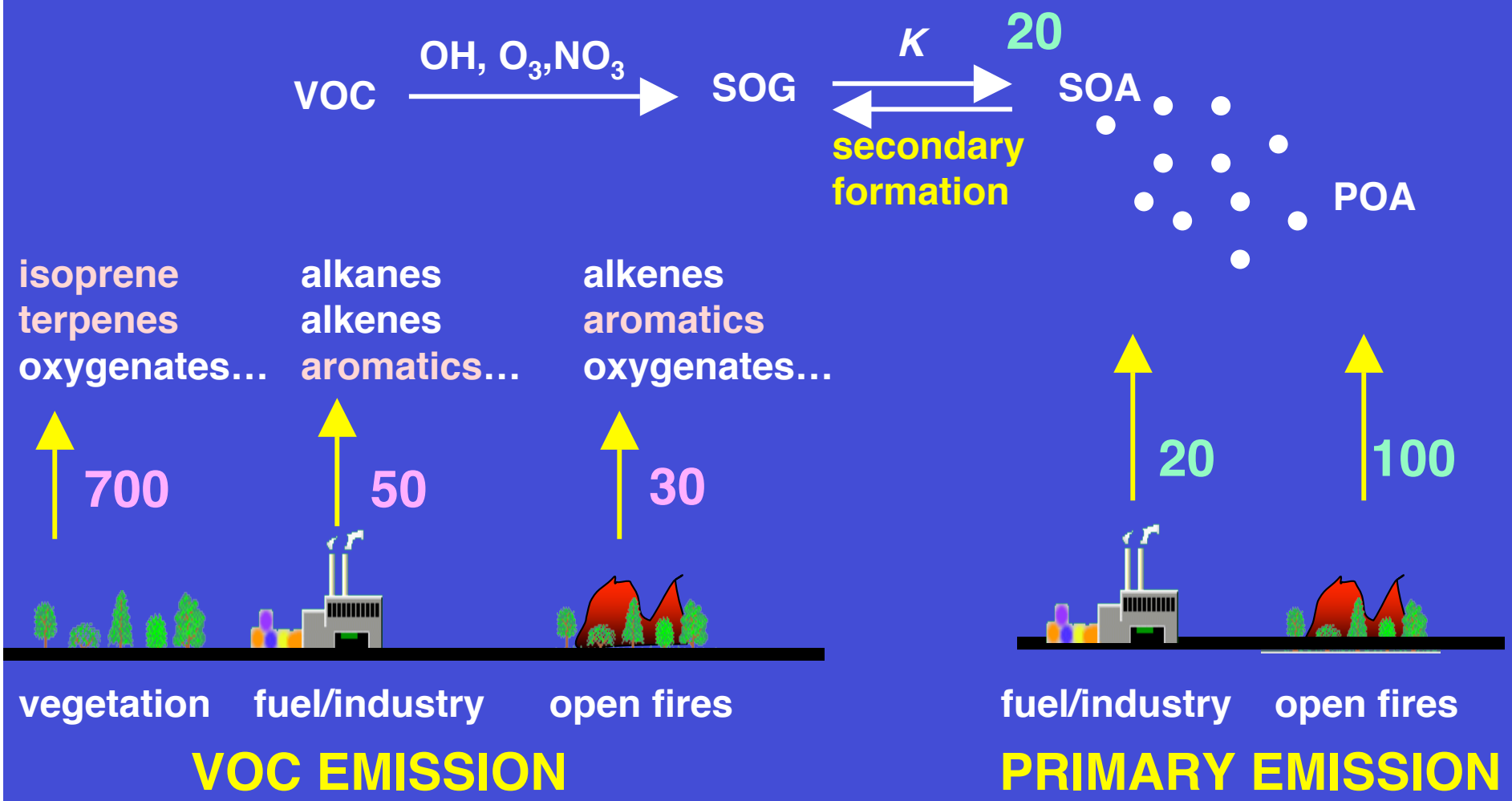
[2] now asst. prof. at University of Nebraska
[3] still trying to get out

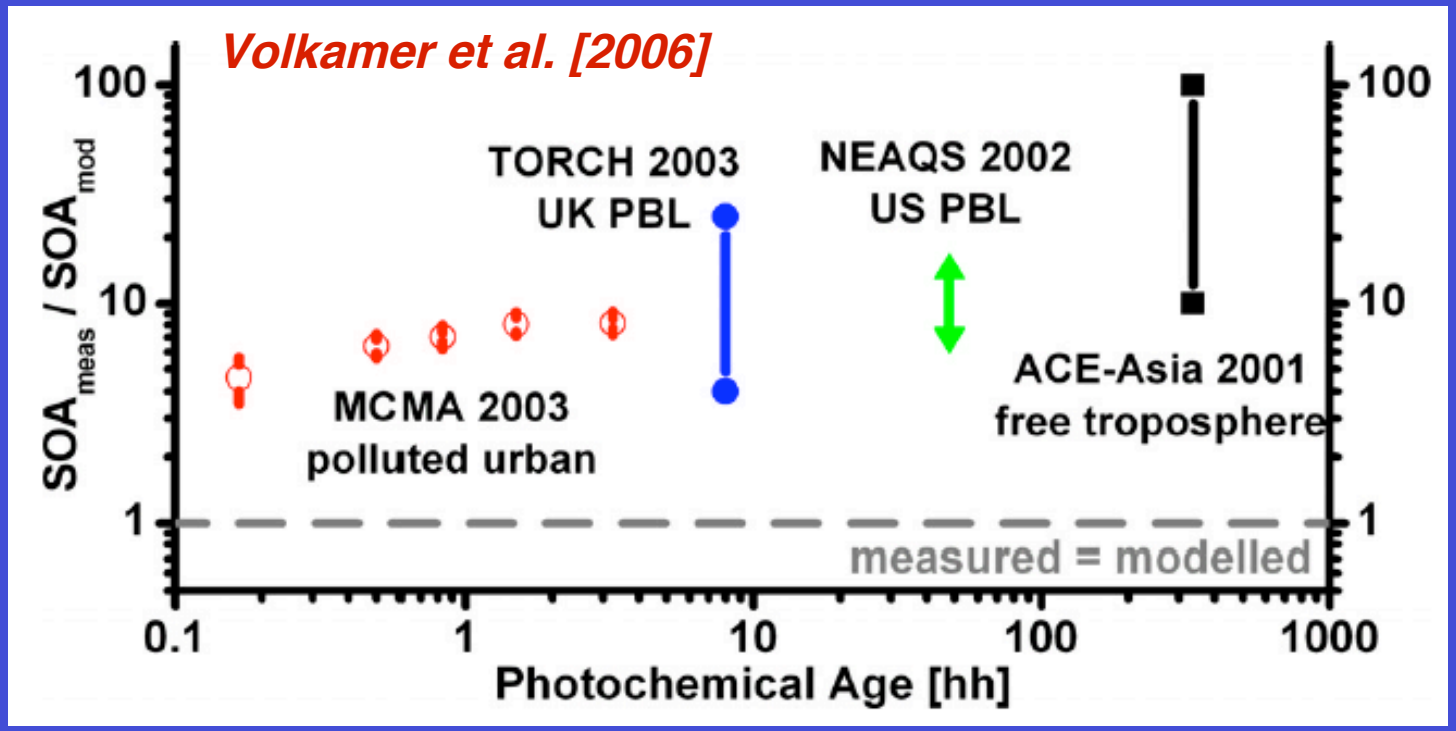
CONVENTIONAL MODELING OF ORGANIC AEROSOL



Global sources in Tg C y^{-1} (standard version of GEOS-Chem model)

…BUT THESE MODELS UNDERESTIMATE OBSERVATIONS

simulated/observed ratios from recent measurement campaigns

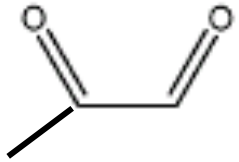


Discrepancy worsens as air masses age; suggests irreversible SOA source missing from the models

IRREVERSIBLE DICARBONYL UPTAKE BY AQUEOUS AEROSOL

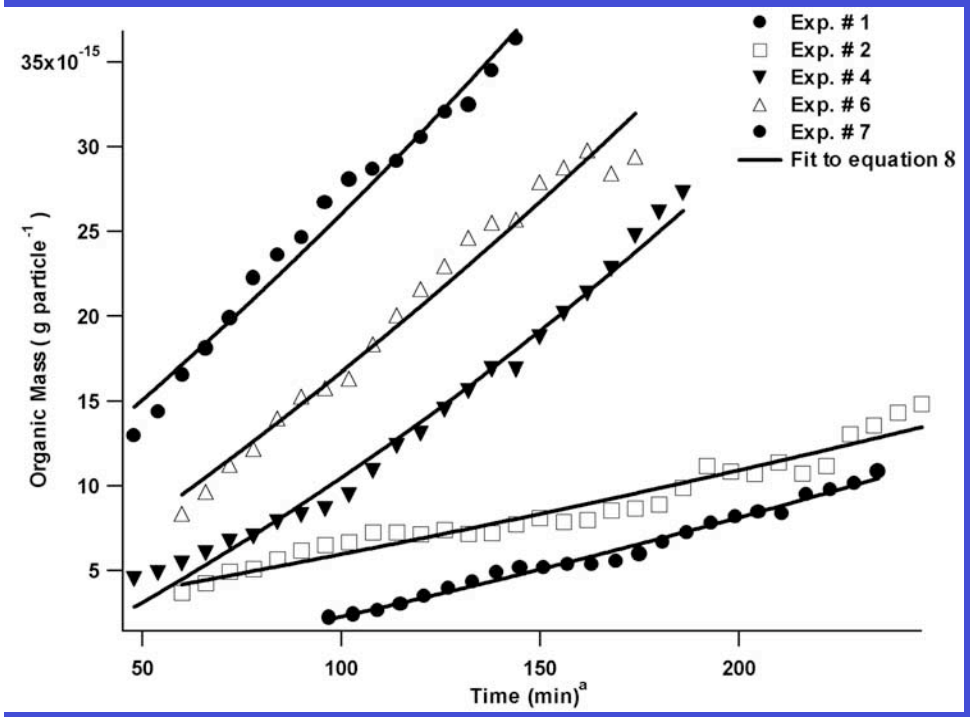
glyoxal

methylglyoxal

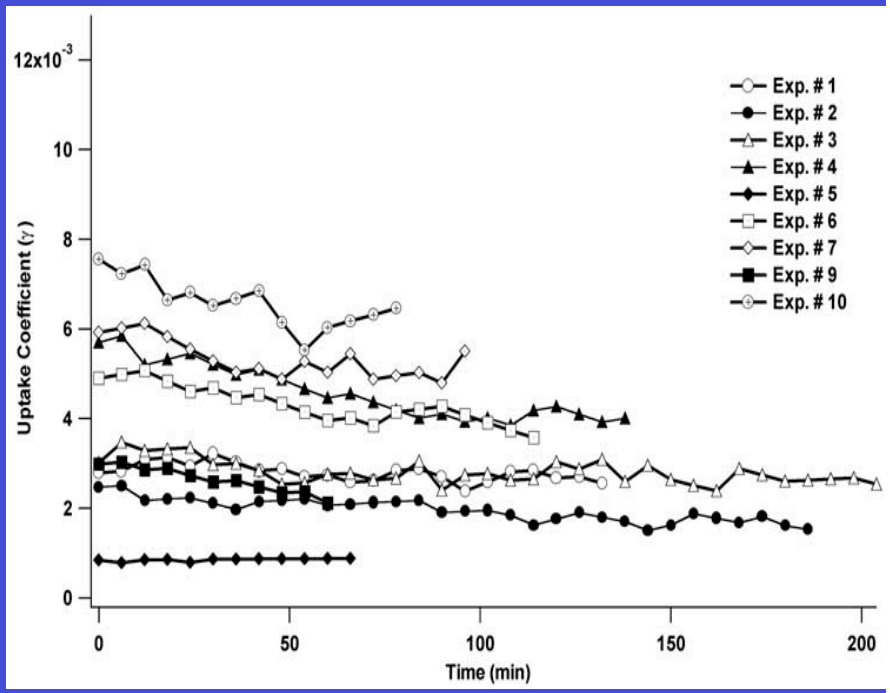


Chamber AMS experiments of glyoxal uptake by Liggio et al. [JGR 2005]

Organic aerosol mass growth with time



Inferred reactive uptake coefficient γ



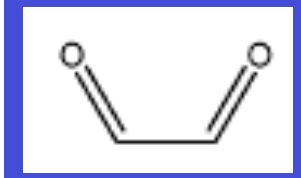
- median $\gamma = 2.9 \times 10^{-3}$ observed for aqueous surfaces; evidence for oligomerization
- similar γ observed for methylglyoxal on acidic surfaces [Zhao et al. ES&T 2006]

POSSIBLE MECHANISMS FOR DICARBONYL SOA FORMATION

GAS

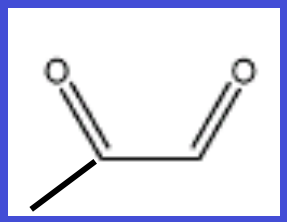
AQUEOUS

glyoxal

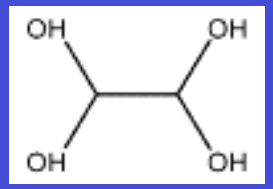


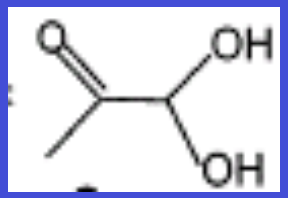
H* ~ 10^5 M atm^{-1}

methylglyoxal



H* ~ 10^3 M atm^{-1}





oligomerization

oxidation

OH

Oligomers

oligomerization

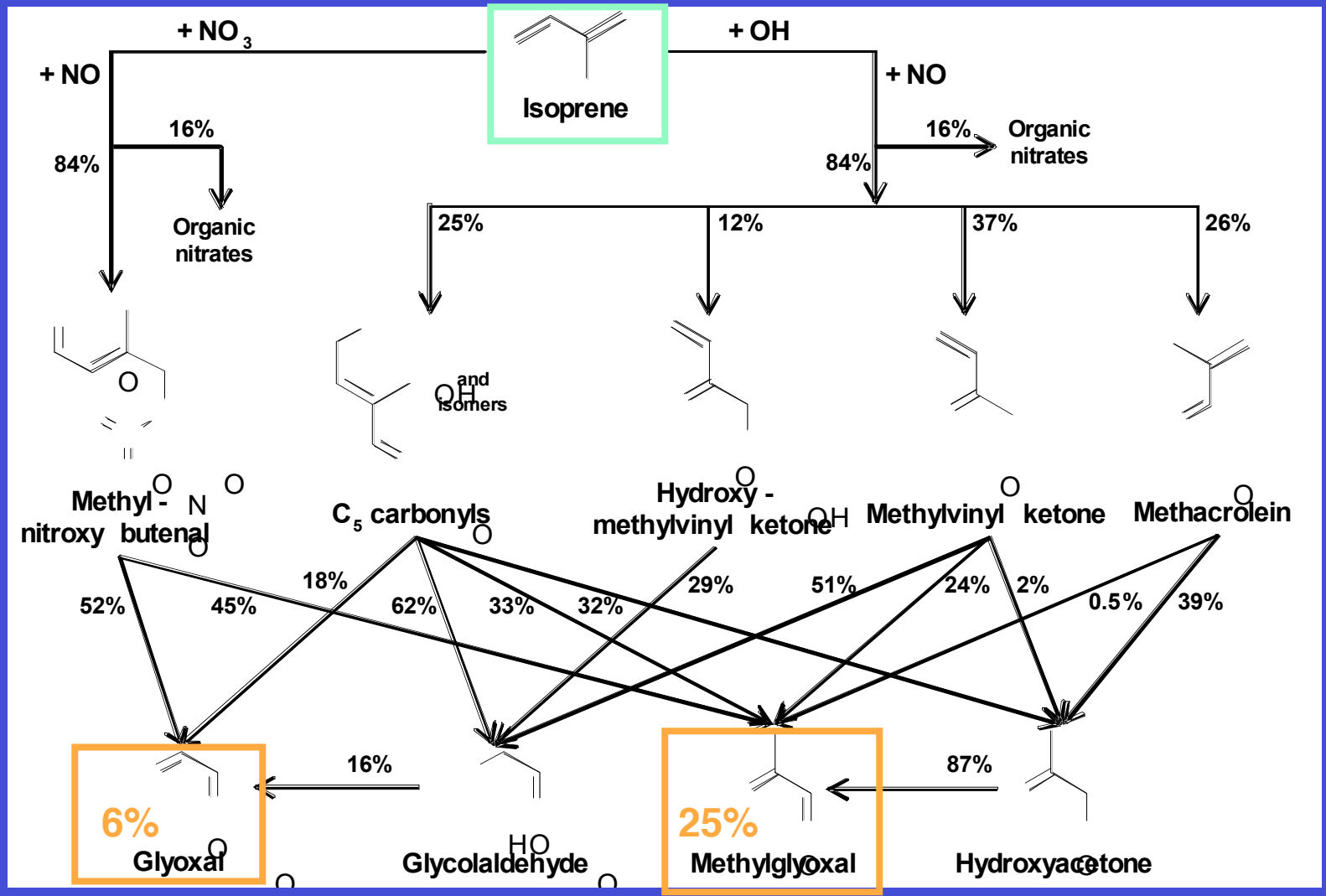
Altieri et al. [2006, 2008]

Organic acids

Schweitzer et al. [1998]
Kalberer et al. [2004]
Liggio et al. [2005a,b]
Hastings et al. [2005]
Zhao et al. [2006]
Loeffler et al. [2006]

Ervens et al. [2004]
Crahan et al. [2004]
Lim et al. [2005]
Carlton et al. [2006, 2007]
Warneck et al. [2005]
Sorooshian et al. [2006, 2007]

GLYOXAL/METHYLGLYOXAL FORMATION FROM ISOPRENE



GEOS-Chem mechanism based on MCM v3.1

molar yields

Fu et al. [JGR, submited]

GLOBAL GLYOXAL BUDGET IN GEOS-Chem

Including reactive uptake by aq. aerosols + clouds with $\gamma = 2.9 \times 10^{-3}$ [Liggio et al., 2005]

CHOCHO			
Production	**Emission [Tg y^{-1}]**	**Molar yield [%]**	**45 [Tg y^{-1}]**
Isoprene	410	6.2	21
Acetylene	6.3	64	8.9
Glyoxal (biomass burning) *	7.7	100	7.7
Ethylene	21	5.7	2.5
Monoterpenes	160	2.8	1.8
Benzene	4.8	25	0.9
Toluene	6.7	16	0.7
Xylenes	4.7	16	0.4
Glycolaldehyde *	5.6	9.9	0.5
Methylbutenol	9.6	5.4	0.3
Loss			**45 [Tg y^{-1}]**
τ = 2.9 h Photolysis			28
Oxidation by OH			6.5
SOA formation			6.4
Dry deposition			2.2
Wet deposition			1.9

Global SOA formation of 6.4 Tg yr^{-1} (1.0 in clear sky + 5.4 in cloud); compare to 16 Tg yr^{-1} from terpenes/isoprene by semivolatile mechanism

Fu et al. [JGR, submited]

GLOBAL METHYLGLYOXAL BUDGET IN GEOS-Chem

Including reactive uptake by aerosols and clouds with $\gamma = 2.9 \times 10^{-3}$

CH_3COCHO			
Production	**Emission [Tg y^{-1}]**	**Molar yield [%]**	**140 [Tg y^{-1}]**
Isoprene	410	25	110
Acetone	57	14	10
Methylglyoxal* (biomass burning)	5.0	100	5.0
$>C_2$ alkenes	31	7.7	4.1
Hydroxyacetone*	4.9	75	3.6
Monoterpenes	160	4.2	3.5
Propane	16	11	2.7
>C3 alkanes	26	3.2	1.0
Toluene	6.7	12	0.7
Xylenes	4.7	23	0.7
Methylbutenol	9.6	6.2	0.5
Loss			**140 [Tg y^{-1}]**
Photolysis			100
SOA formation			16
Oxidation by OH			15
Wet deposition			1.8
Dry deposition			1.7

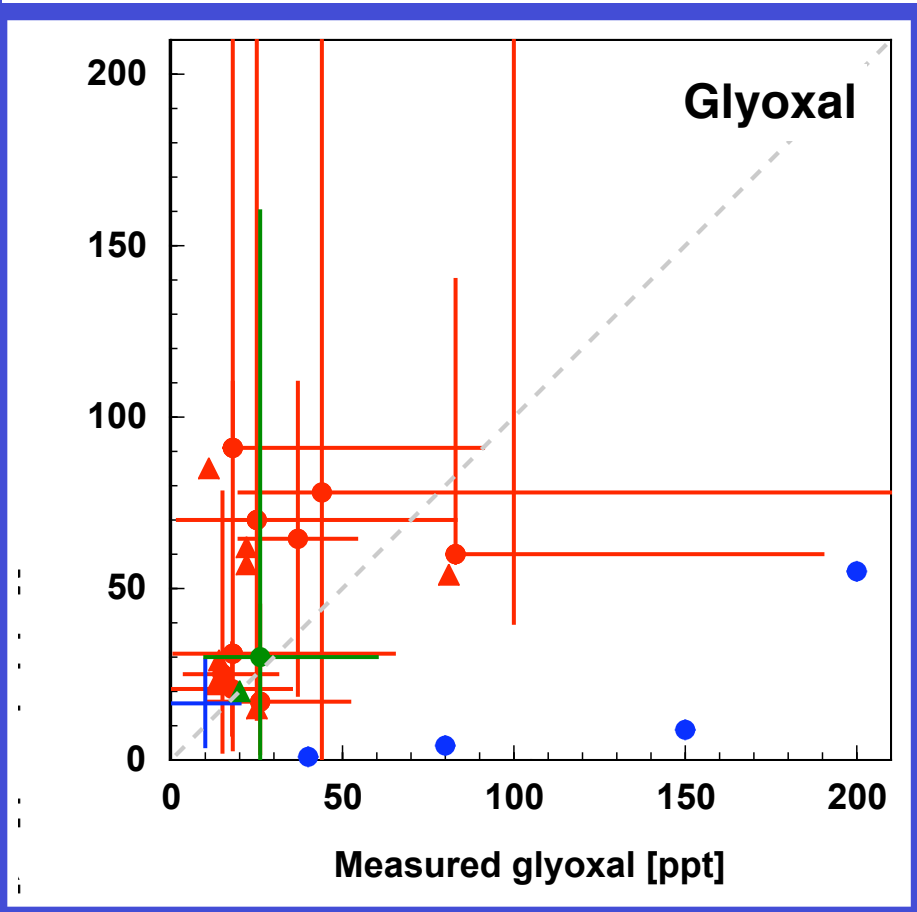
$\tau = 1.6$ h

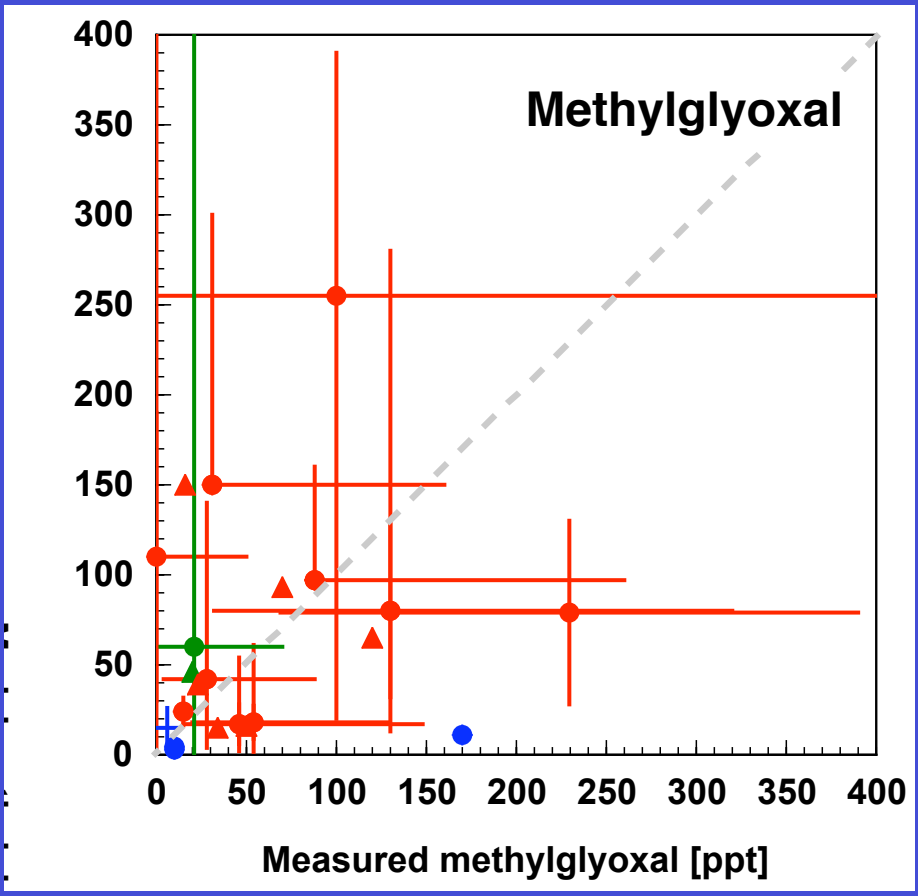
Global SOA formation of 16 Tg yr^{-1} (2 in clear sky + 14 in cloud); compare to 16 Tg yr^{-1} from terpenes/isoprene by semivolatile mechanism

Fu et al. [JGR, submited]

MODEL COMPARISON TO IN SITU OBSERVATIONS

Continental boundary layer (all northern midlatitudes summer)
Continental free troposphere
Marine boundary layer

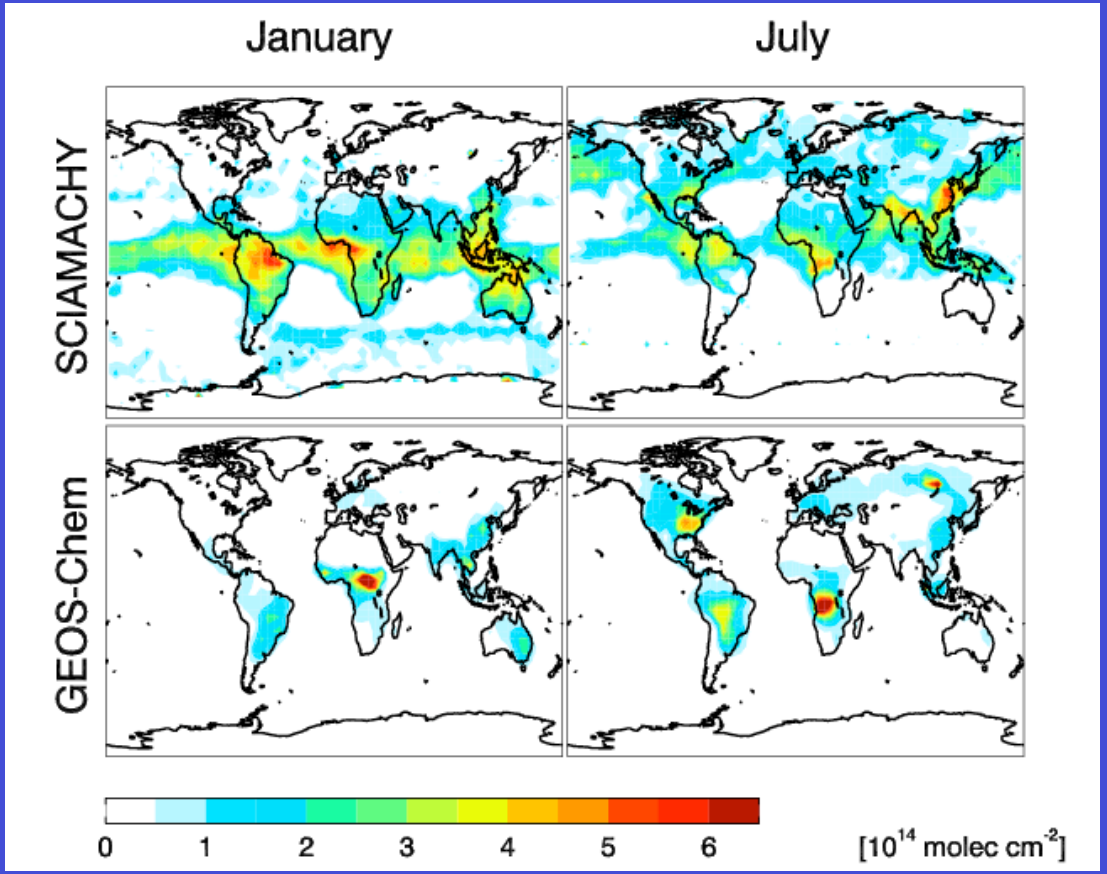




Indication of a missing marine source in the model

Fu et al. [JGR, submited]

SCIAMACHY SATELLITE OBSERVATION OF GLYOXAL



- General spatial pattern reproduced over land, SCIAMACHY is 50% higher than model
- SCIAMACHY sees high values over oceans correlated with chlorophyll: unidentified marine source?

100 pptv glyoxal in marine boundary layer would yield ~1 μg C m^{-3} SOA; could contribute to observed OC aerosol concentrations in marine air

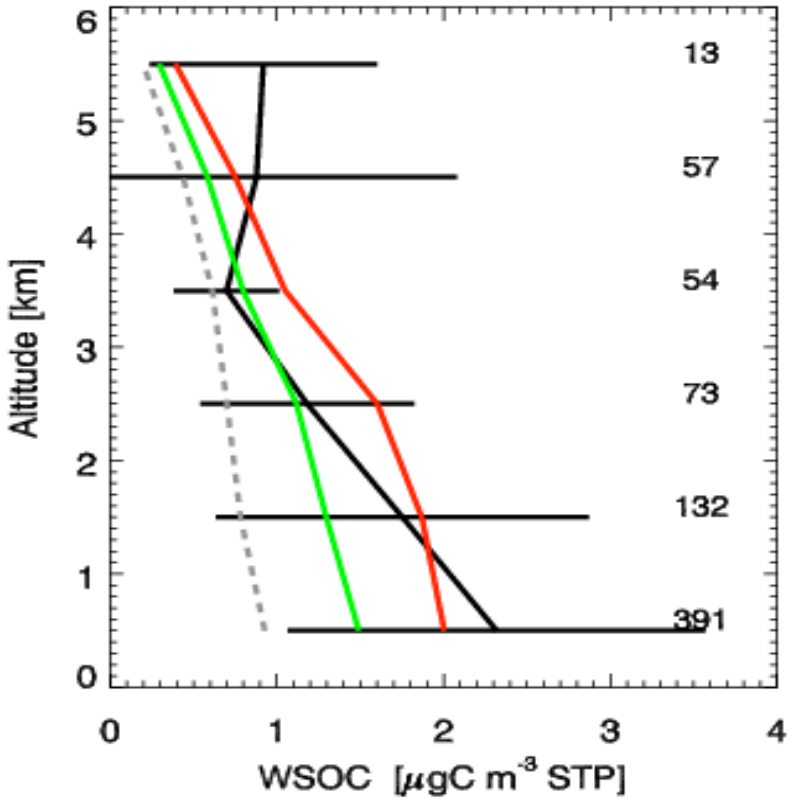
Fu et al. [JGR, submited]

SIMULATION OF WSOC AEROSOL OVER EASTERN U.S.

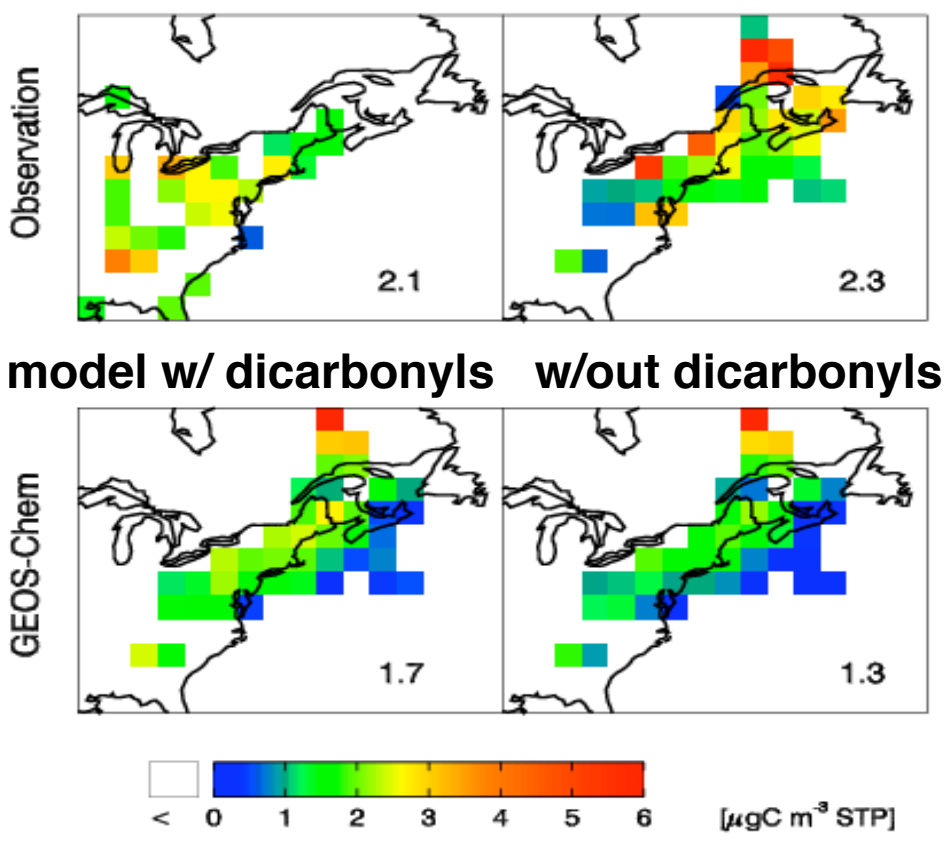
Water-soluble OC (WSOC) aerosol observations by Rodney Weber (GIT) from NOAA aircraft during ICARTT campaign out of Portsmouth, NH (Jul-Aug 04)

biomass burning plumes excluded

- Observed
- Model w/ dicarbonyl SOA added
- Model w/ standard SOA
- Model hydrophilic primary OA

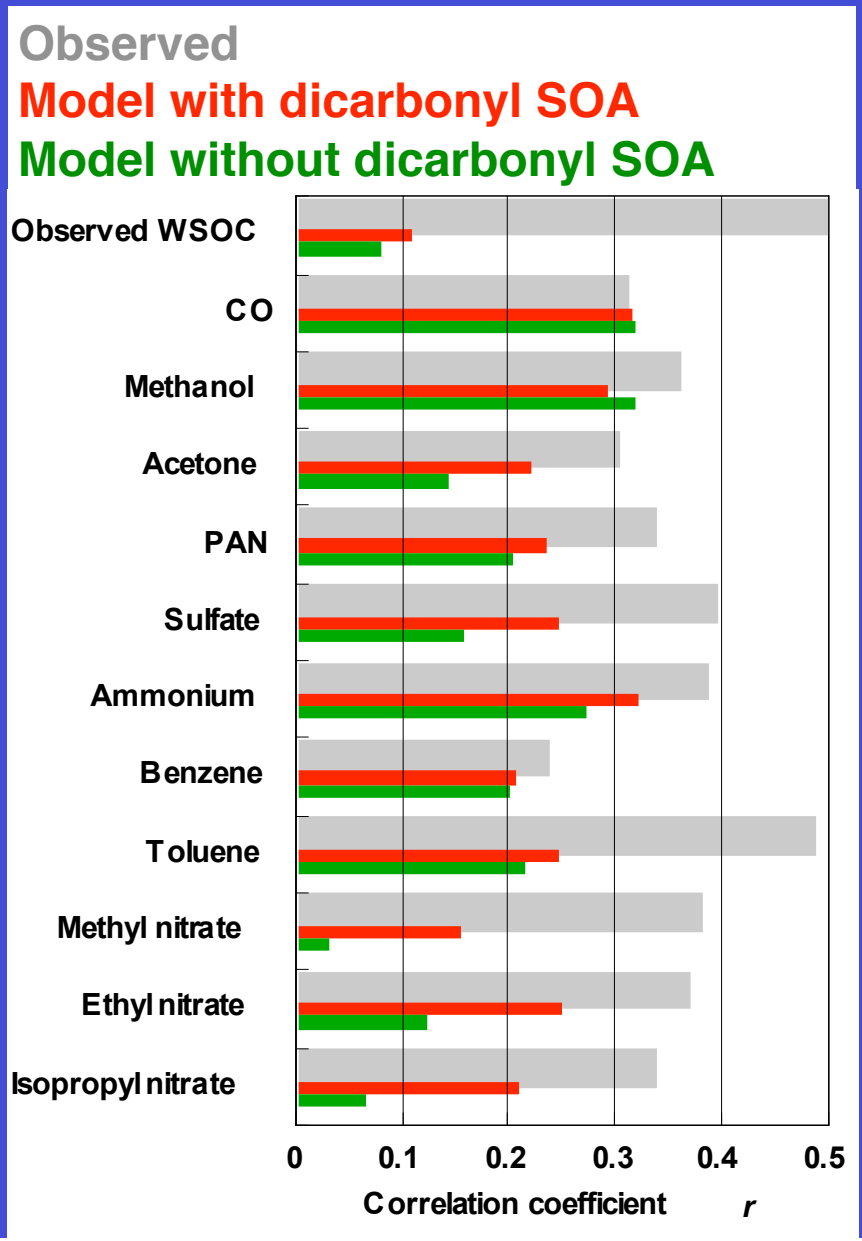


Boundary layer data (<2 km)



Fu et al., in prep.

CORRELATIONS OF FREE TROPOSPHERIC WSOC WITH OTHER VARIABLES MEASURED ON NOAA AIRCRAFT



- WSOC is observed to correlate with
- toluene and methanol (anthro+bio?)
- sulfate (aqueous-phase production?)
- alkyl nitrates (photochemistry?)

- Model does not reproduce observed WSOC variability but does better with correlations, particularly when dicarbonyl SOA is included (sulfate, alkyl nitrates)

Fu et al., in prep.

EXPLAINING PERSISTENT OBSERVATIONS OF NEUTRALIZED SULFATE IN UPPER TROPOSPHERE

$DMS, SO_2 \rightarrow H_2SO_4$

NH_3

Is NH_3 retained or released when cloud droplets freeze?

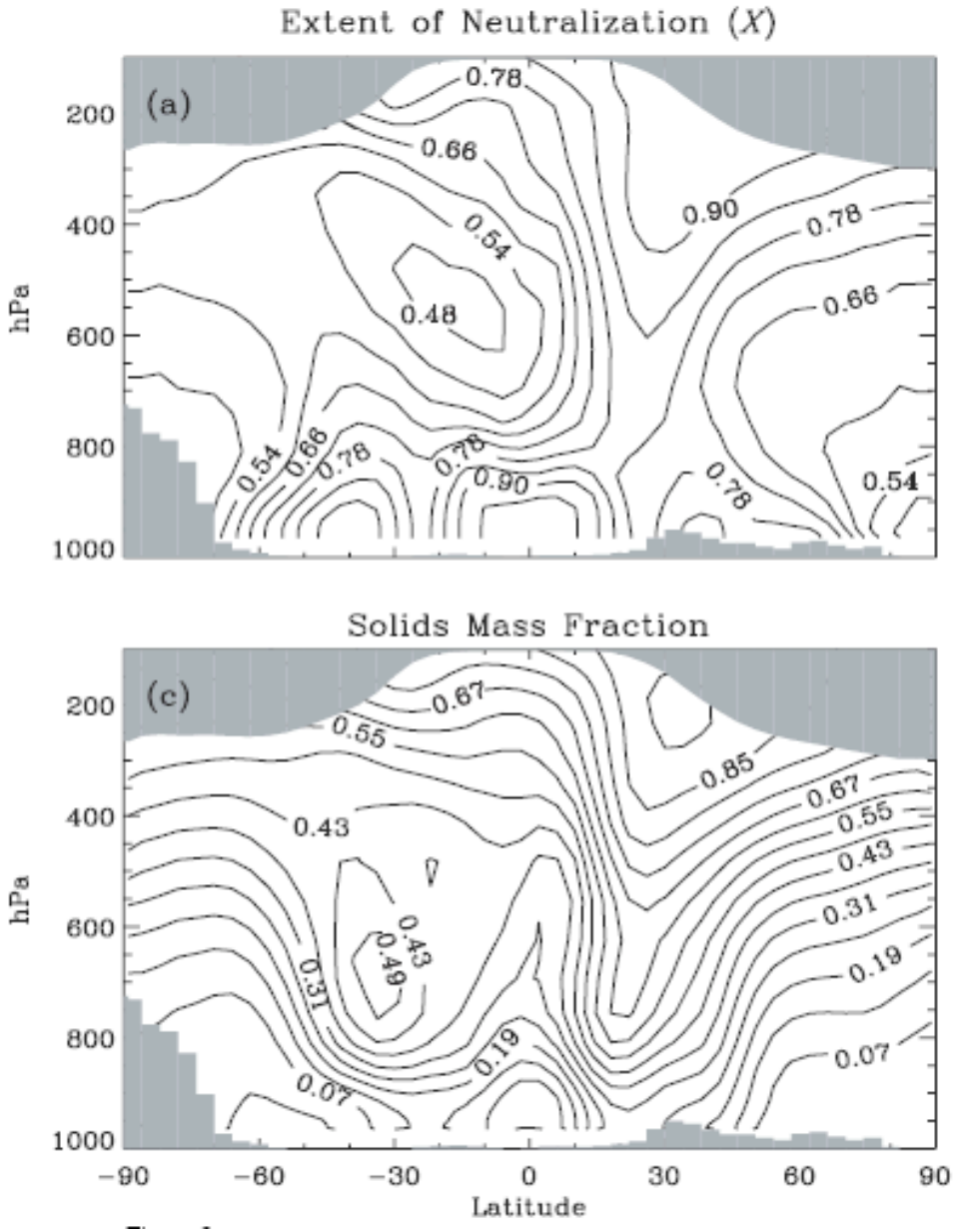
efficient scavenging of aerosol, HNO_3, NH_3, some SO_2 by liquid droplets

Precipitation removal

DMS, SO_2
Sulfate aerosol
NH_3
HNO_3

Lab data indicate NH_3 retention efficiency of 10^{-4}-10^{-2}; , would allow efficient release of NH_3 to neutralize upper tropospheric aerosol

IMPLICATIONS FOR SULFATE NEUTRALIZED FRACTION (*X*) AND AEROSOL PHASE



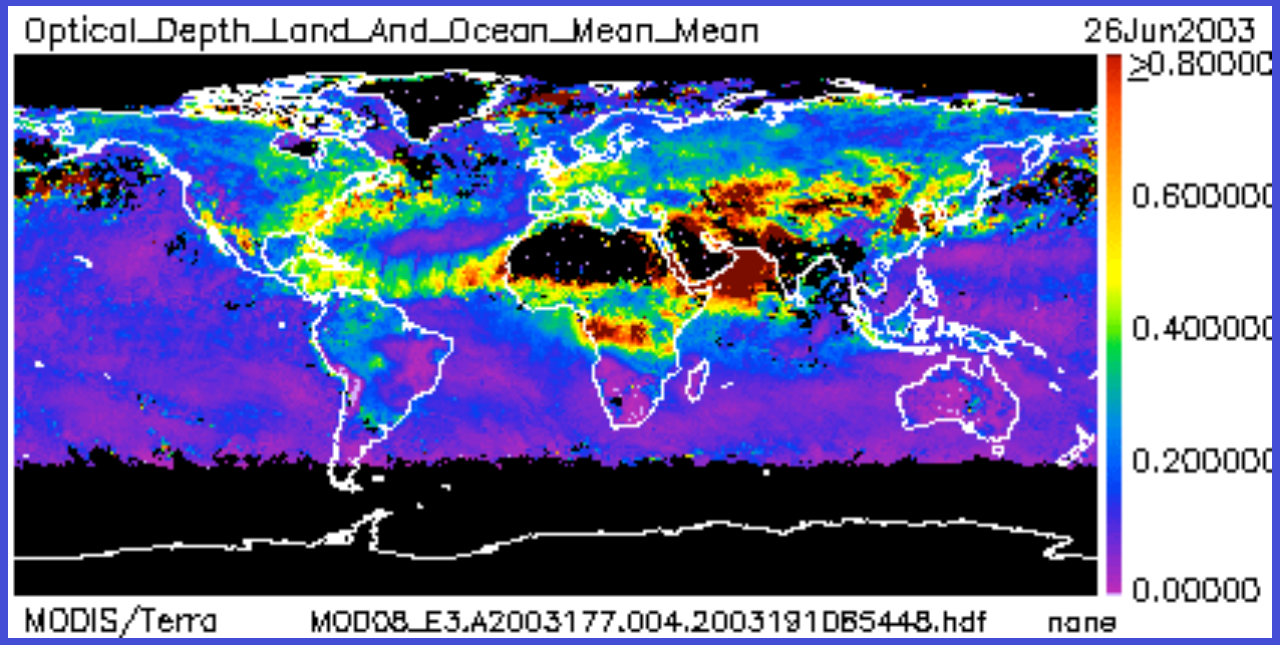
Annual zonal mean GEOS-Chem model results in an ammonium-sulfate simulation including hysteresis of phase transitions and NH_3 retention efficiency of 0.05 upon cloud freezing

Upper tropospheric sulfate is mostly neutralized and solid! Implications for atmospheric chemistry, cirrus formation…

Wang et al. [JGR, submitted]

INTERPRETING SATELLITE AEROSOL DATA: HOW DO WE GO BEYOND PRETTY PICTURES?

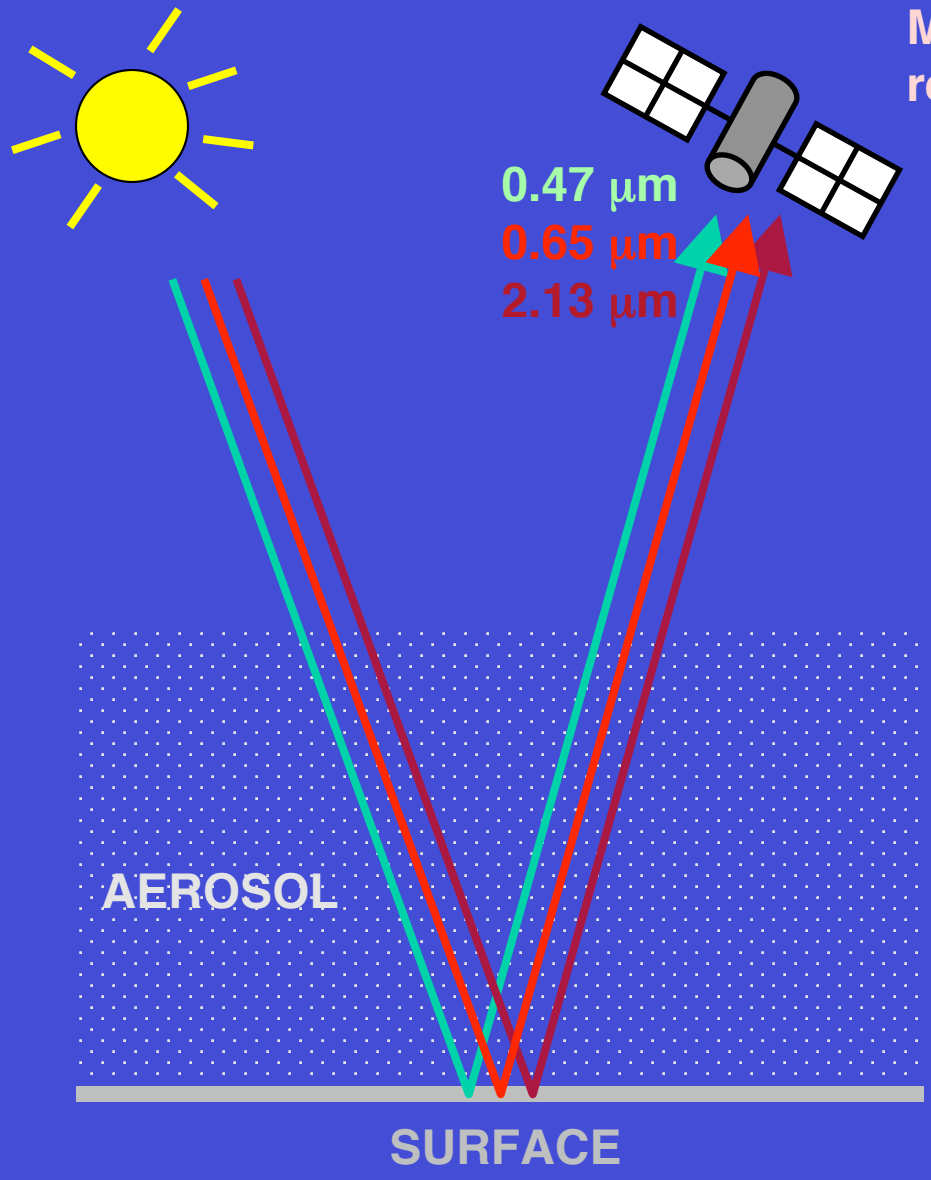
MODIS 0.47 μm aerosol optical depth (June 2003)



How can we use satellite data to better quantify aerosol sources and processes through comparison to models? Need

1. **improved surface reflectance data over land**
2. **model simulation of top-of-atmosphere reflectance in satellite field of view**

IMPROVING MODIS SATELLITE RETRIEVALS OF AEROSOL OPTICAL DEPTHS OVER LAND



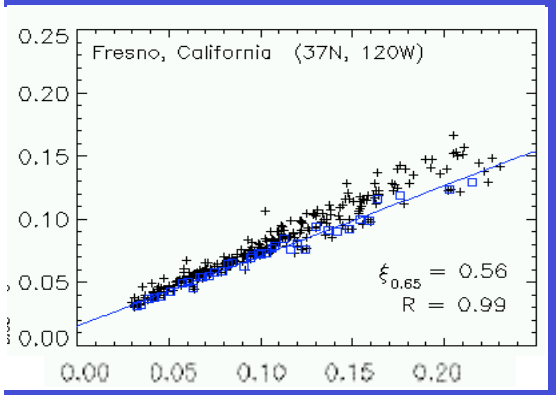
Drury et al. [JGR, subnmitted]

MODIS measures top-of-atmosphere (TOA) reflectance in several wavelength channels

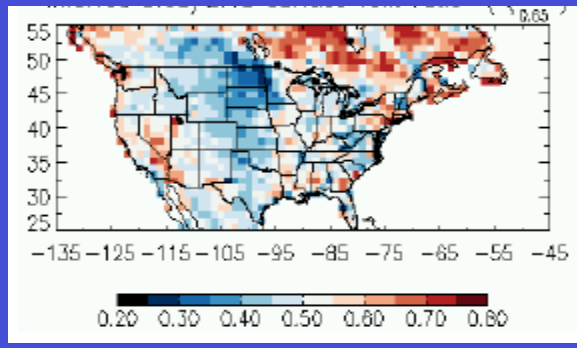
- **Interpretation of TOA reflectance in terms of AOD requires assumptions on surface reflectance, aerosol optical properties**
- **Use TOA reflectance at 2.13 μm (transparent atmosphere) to derive surface reflectance**
- **MODIS operational algorithm relies on general assumptions for 0.47/2.13 and 0.65/2.13 surface reflectance ratios; we improve by deriving those locally using lower envelope in scatterplots of 0.65 vs. 2.13 MODIS TOA reflectance data**
- **MODIS operational algorithm relies on general categories for aerosol optical properties; improve by using local GEOS-Chem model data**

GEOS-Chem SIMULATION OF MODIS TOP-OF-ATMOSPHERE REFLECTANCE (JUL-AUG 2004)

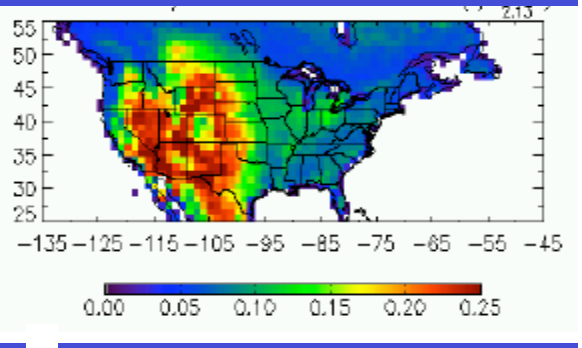
0.65 vs. 2.13 μm TOA reflectance



0.65/2.13 surface reflectance ratio

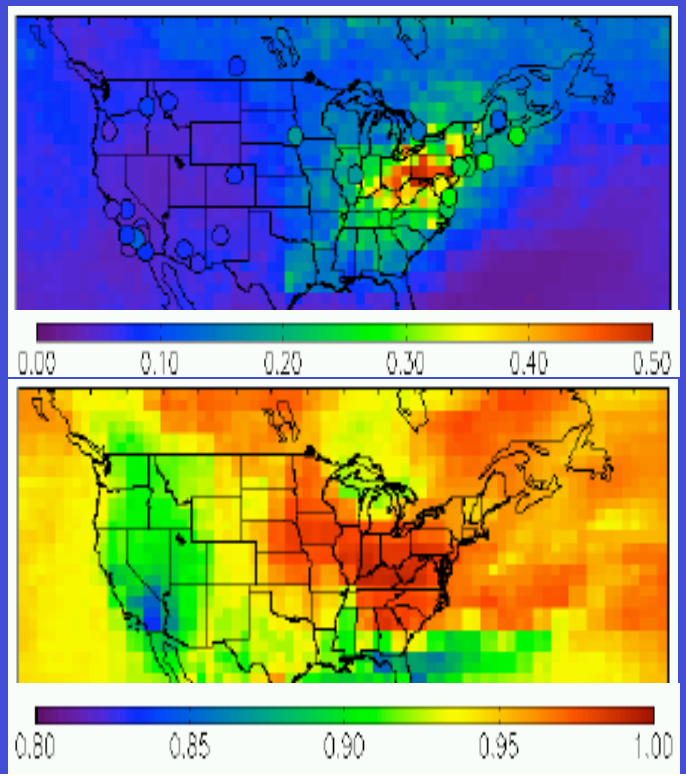


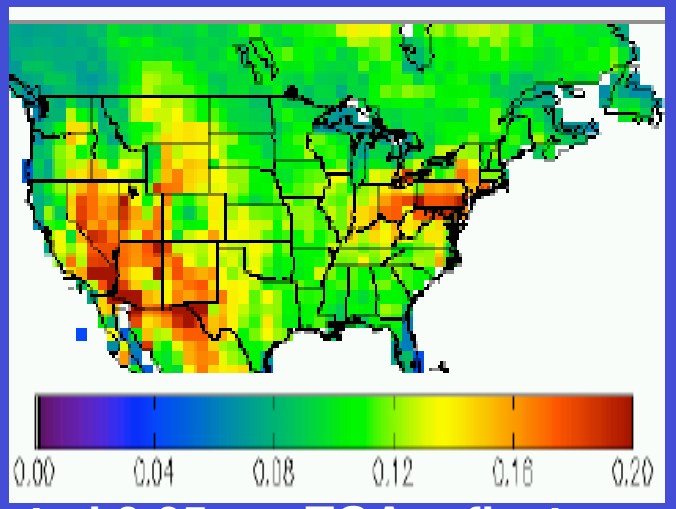
2.13 μm TOA reflectance



GEOS-Chem 0.65 μm AOD (AERONET In circles)

GEOS-Chem 0.65 μm single-scattering albedo





Simulated 0.65 μm TOA reflectance

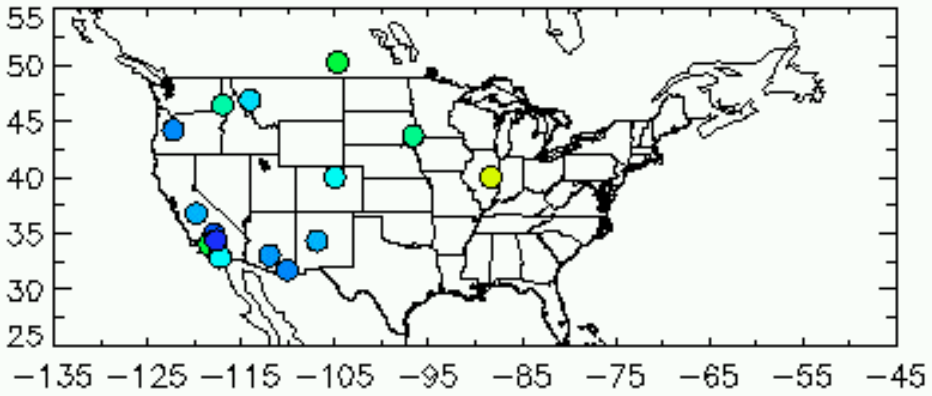
Drury et al. [JGR, submitted]

IMPROVED AOD RETRIEVAL OVER CENTRAL/WESTERN U.S.

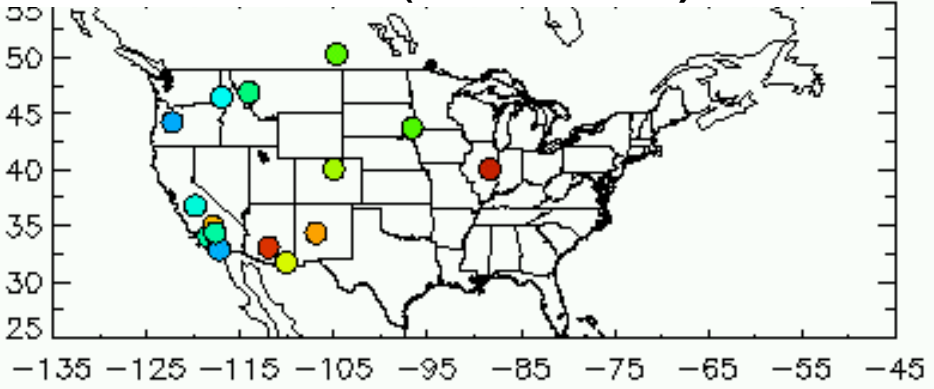
by fitting model TOA reflectances to MODIS observations

MODIS vs. AERONET 0.47 μm AODs (Jul-Aug 2004)

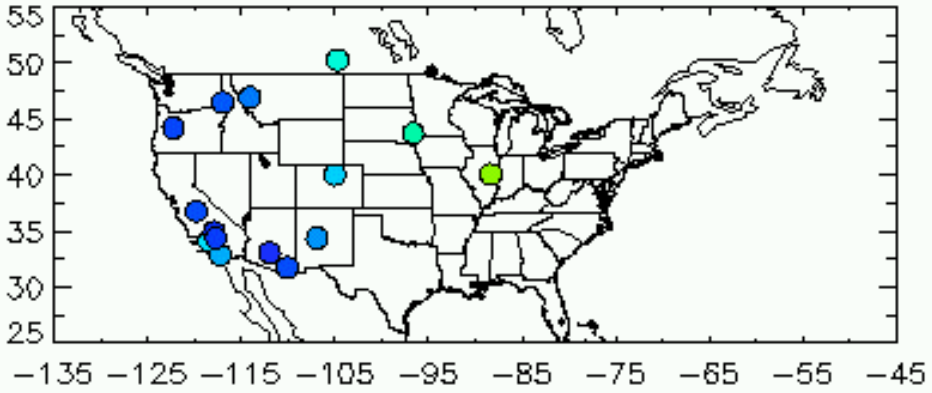
AERONET



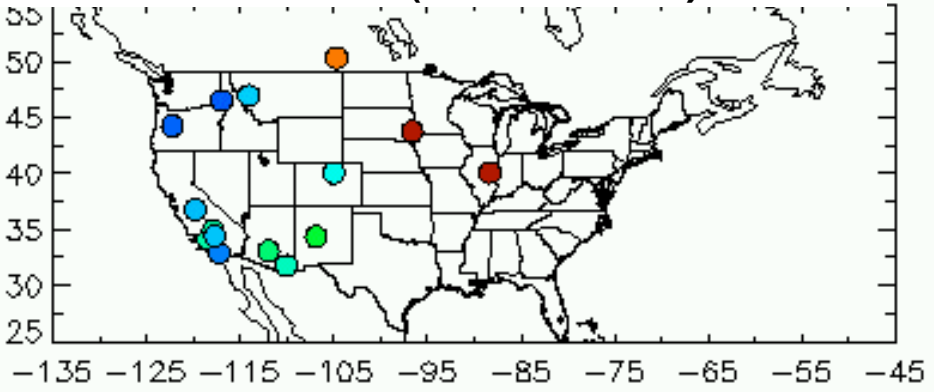
MODIS (collection 5)

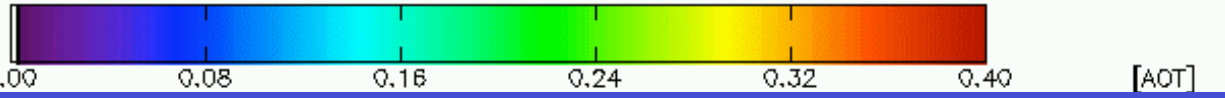


MODIS (this work)



MODIS (collection 4)





Drury et al. [JGR, submitted]

NASA/ARCTAS 2008 AIRCRAFT CAMPAIGN TO THE ARCTIC

Two deployments: April (Fairbanks) and June-July (Cold Lake, Alberta)

Four research themes: (1) transport of mid-latitudes pollution to Arctic, (2) boreal forest fires, (3) aerosol radiative forcing, (4) chemical processes

DC-8: in situ chemistry and aerosols

Ceiling 37 kft, range 4000 nmi, endurance 9 h
Payload: O_3, H_2O, CO, CO_2, CH_4, NO_x and HO_x chemistry, BrO, mercury, NMVOCs, halocarbons, SO_2. HCN/CH_3CN, actinic fluxes, aerosol composition, aerosol mass and number concentrations, aerosol physical and optical properties, remote ozone and aerosol

P-3: radiation and in situ aerosols

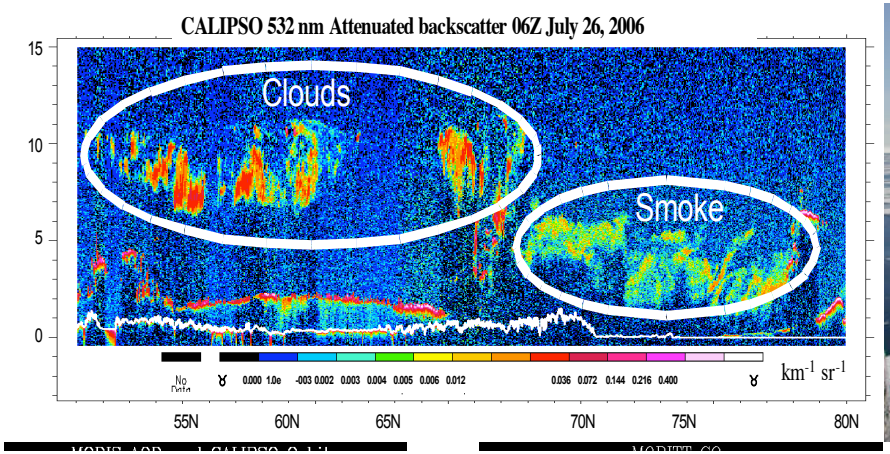
Ceiling 30 kft, range 3800 nmi, endurance 8 h
Payload: optical depth, radiative flux, radiance spectra, aerosol composition, black carbon

B-200: aerosol remote sensing and CALIPSO validation

Ceiling 32 kft, range 800 nmi, endurance 3.5 h
Payload: High Spectral Resolution Lidar (HSRL)
Research Scanning Polarimeter (RSP)

ARCTAS Science Theme 3: Aerosol radiative forcing

CALIPSO clouds and smoke



C. Trepte, LaRC

Arctic haze

MISR true-color fire plume

R. Kahn, JPL

- What is the regional radiative forcing from Arctic haze, fire plumes?
- How does this forcing evolve during plume aging?
- What are the major sources of soot to the Arctic?
- How does soot deposition affect ice albedo?

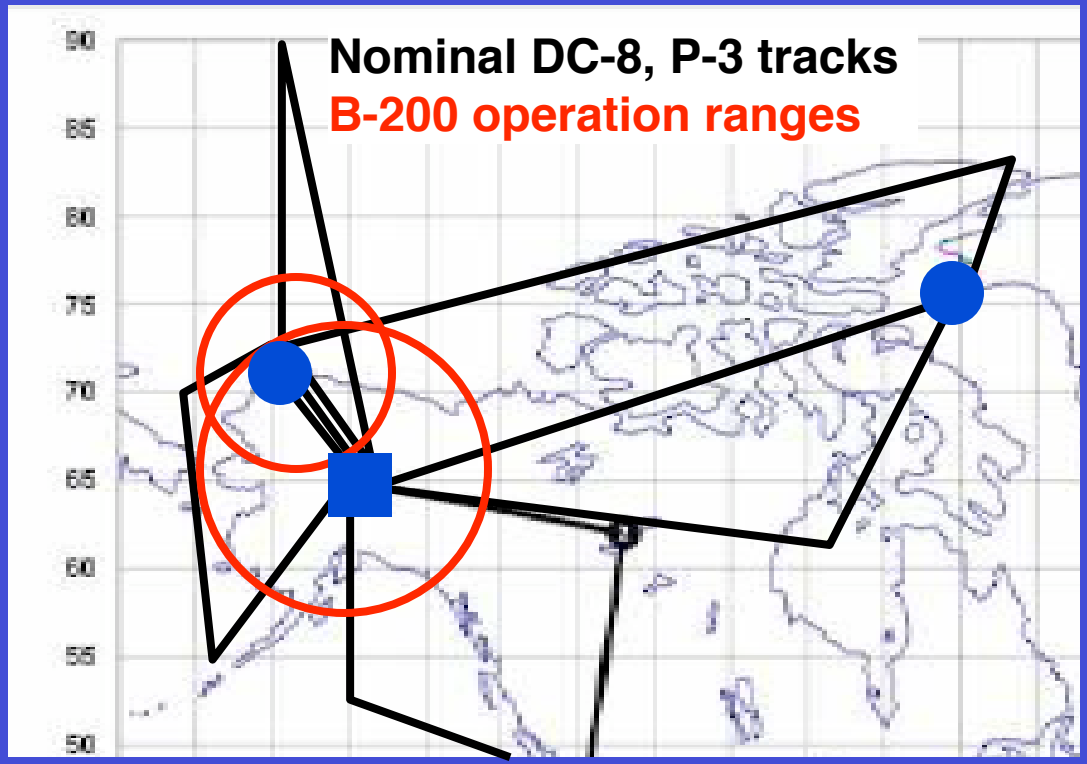
Satellite capabilities:

- UV/Vis/IR reflectances (Cloudsat, MODIS, MISR, OMI)
- multi-angle sensing (MISR)
- lidar (CALIPSO)

Aircraft added value:

- detailed in situ aerosol characterization
- remote sensing of radiances, fluxes
- BRDFs

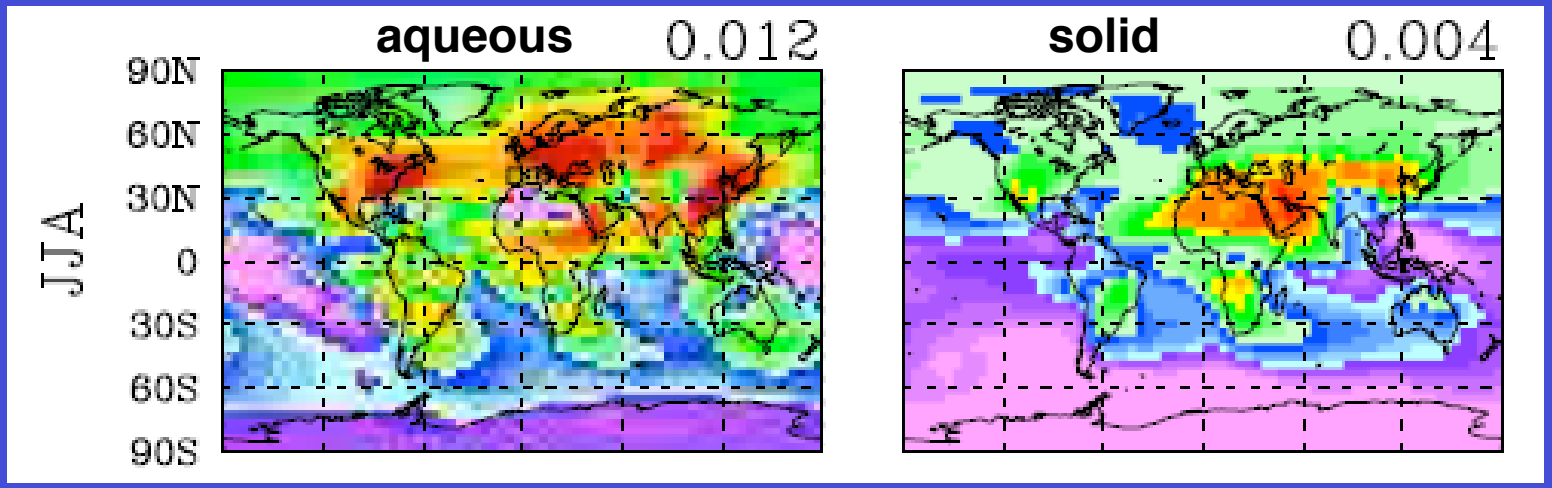
ARCTAS SPRING DEPLOYMENT



- Deployment period: April 1-21
- About 70 flight hours for each aircraft
- Primary base: Fairbanks. Secondary bases: Barrow (B-200), Thule (DC-8, P-3)
- Several flights to involve collaboration with ISDAC

EFFECT OF PHASE TRANSITIONS ON DIRECT SULFATE RADIATIVE FORCING

GEOS-Chem anthropogenic sulfate optical depth (0.55 μm)

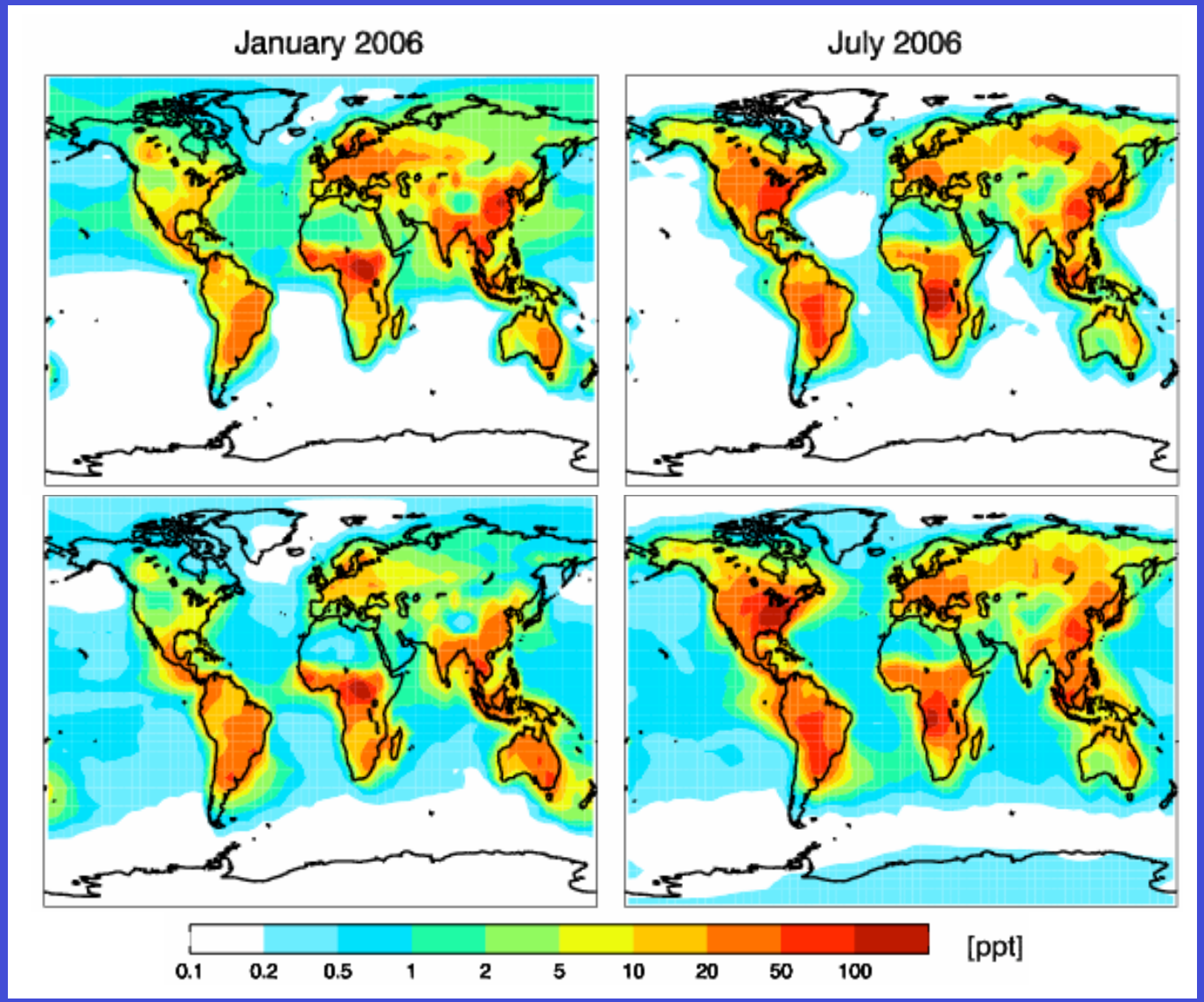


Direct anthropogenic sulfate radiative forcing (W m^{-2})

Base simulation with hysteresis	-0.25
CRH=DRH (upper branch of hysteresis loop)	-0.24
DRH=CRH (lower branch of hysteresis look)	-0.26
CRH=0 (no crystallization)	-0.27

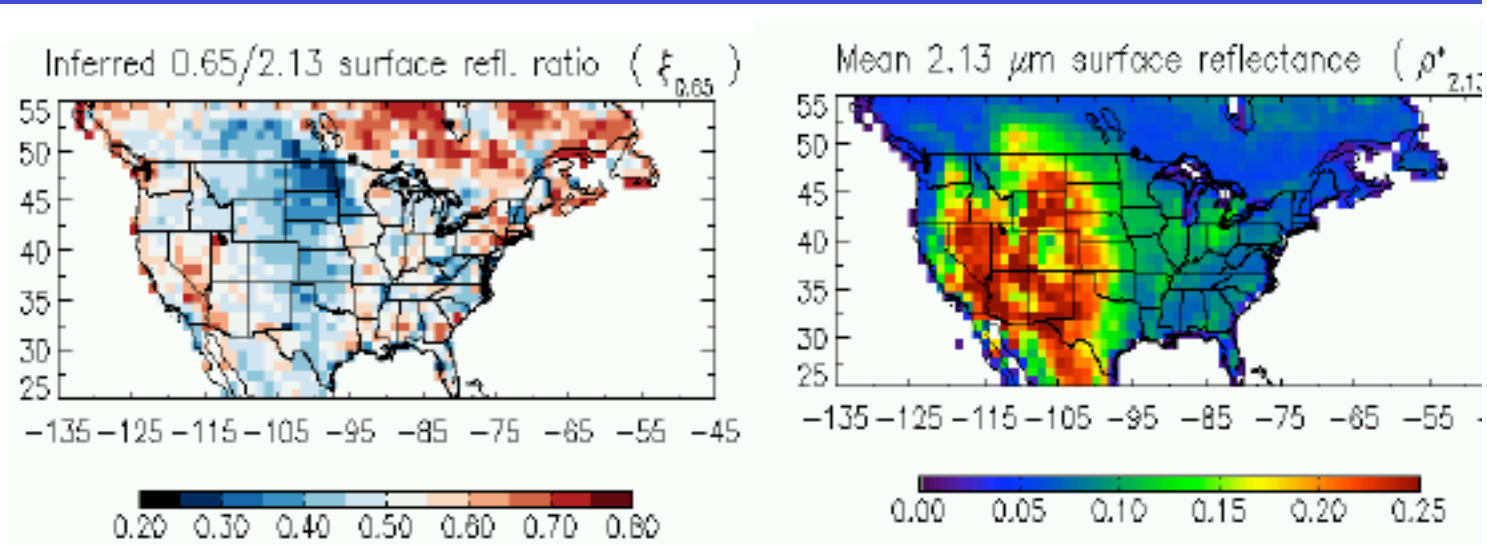
Wang et al. [JGR, submitted]

SIMULATED SURFACE CONCENTRATIONS



- Highest concentrations in regions of biomass burning regions, active vegetation
- ~1 ppt background from acetylene (glyoxal), acetone (methylglyoxal)

Fu et al. [JGR, submited]


Inferred 0.65/2.13 surface refl. ratio ($\xi_{0.65}$)
55
50
45
40
35
30
25
−135 −125 −115 −105 −95 −85 −75 −65 −55 −45
0.20 0.30 0.40 0.50 0.60 0.70 0.80
Mean 2.13 μm surface reflectance ($\rho^*_{2.1}$
55
50
45
40
35
30
25
−135 −125 −115 −105 −95 −85 −75 −65 −55
0.00 0.05 0.10 0.15 0.20 0.25